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ADSORPTION MATERIAL FOR COLLECTING URANIUM
[Uran saishuyou kyuuchakuzai]

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TITLE (54) : ADSORPTION MATERIAL FOR
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1. Title of the Invention

Adsorption material for collecting uranium

2. Claim

An adsorbent material for collecting uranium wherein a dispersion comprising 1 or more species of powdery uranium adsorbing material selected from a group comprising titanic acid, titanates, lead sulfide, galena, and basic zinc carbonate, an acrylonitrile-based polymer containing 50% by weight or more acrylonitrile, and a good solvent for an acrylonitrile-based polymer, with the content having a ratio of 5-95/95-5 by weight of uranium adsorbing material/acrylonitrile-based polymer, is added to a poor solvent for an acrylonitrile-based polymer so as to be coagulated.

3. Detailed Description of the Invention

The present invention relates to an adsorbent material for collecting uranium in order to collect uranium from a solution where dissolved uranium is present in trace amounts.

Conventionally, titanic acid, titanate, lead sulfide, and basic zinc carbonate, for example, have been known as materials to which uranium is selectively adsorbed from a solution that contains a low concentration of uranium, such as the leach liquor of a low-grade uranium ore. Alone, however, these materials have low physical strength. For example, when used in a column method, they have the

* Numbers in the margin indicate pagination in the foreign text.

disadvantage of changing into a fine powder, which then drains away.

In order to overcome this disadvantage, there are materials for adsorption such as a titanated polyvinyl alcohol obtained by reacting polyvinyl alcohol with titanic acid, and an activated carbon-titanium hydride complex obtained by causing titanic acid to be adsorbed onto active carbon, and other complex materials, for example. However, in each case it is difficult to cause a high concentration of titanic acid to be contained in the substrate, so the adsorption rate (amount of uranium adsorbed per 1 g of adsorption material) is low, thus presenting a problem for the economic recovery of uranium.

Keenly aware of this situation, the inventors conducted a series of diligent investigations to improve a complex adsorption material so as to effectively recover uranium from a solution where dissolved uranium is present in trace amounts; as a result, they succeeded in obtaining a complex adsorption material by treating a powdery uranium adsorbing material with an acrylonitrile-based polymer, in order to improve strength without sacrificing the adsorption-active surface area of the uranium adsorbing material.

Specifically, the present invention offers an adsorbent material for collecting uranium that has many characteristics, such as the fact that a dispersion (hereunder referred to as a "slurry dope") comprising 1 or more species of powdery uranium adsorbing material selected from a group comprising titanic acid, titanates, lead sulfide, galena, and basic zinc carbonate, an acrylonitrile

(hereunder abbreviated as AN)-based polymer containing 50% by weight or more AN, and a good solvent for an AN-based polymer, with the content having a ratio of 5-95/95-5 by weight of uranium adsorbing material/AN-based polymer, is added to a poor solvent (hereunder referred to as a "coagulation solution") for an acrylonitrile-based polymer so as to be coagulated. The invented adsorption material further has the characteristics of being a complex adsorption material in which an AN-based polymer has a large surface area due to wet coagulation, and contains a large amount of uranium adsorbing material. Other characteristics are that, because a uranium adsorbing material-complex is formed at a low temperature by the wet method, the uranium adsorbing material does not undergo any chemical changes; and because the uranium adsorbing material is a fine grain with wide absorption surface area that is contained in an AN-based polymer, it has a better-than-expected absorption performance; and still furthermore, it is possible for the amount of uranium adsorbing material contained in the AN-based polymer to be large in relation to the weight of the adsorption material; as well as other characteristics.

Furthermore, various modes are possible for bringing the invented adsorption material into contact with a solution where dissolved uranium is present, according to the mode of use, such as placing the adsorption material in a metal net and immersing this in the solution where dissolved uranium is present, packing it into a

column as an adsorption tower through which the solution containing dissolved uranium is passed, or forming the adsorption material into a mat and using it as an adsorption pad, for example. A fibrid adsorption material is particularly preferred, in which shearing force is imparted during the congealing of the AN-based polymer.

An AN-based polymer used in the present invention to obtain an adsorption material means an AN homopolymer or a copolymer that contains at least 50% by weight or more AN. Examples of a monomer that is copolymerizable with AN include vinyl acetate, acrylic acid ester, styrene, vinyl chloride and vinyl monomers that have a sulfonate group. It is acceptable to use 1, 2, or more species of these monomers.

As a uranium adsorbing material, it is possible to use 1 or more species selected from the group comprising ortho-titanic acid (Ti(OH)_4), metatitanic acid (TiO(OH)_2), a titanate (CaTiO_3 , BaTiO_3 , SrTiO_3 , FeTiO_3 , $\text{Fe}_2(\text{TiO}_3)_3$), lead sulfide (PbS), galena, and basic zinc carbonate (ZnCO_3 , Zn(OH)_2). It is necessary for the uranium adsorbing material to be in the form of a powder, in order to have a large surface area, with the grain diameter being preferably 1 mm or less.

The weight ratio of powdery uranium adsorbing material/AN-based polymer is 5-95/95-5, preferably 10-90/90-10.

Either an organic solvent or inorganic solvent can be used as the good solvent for the AN-based polymer, as long as it is able to dissolve the AN-based polymer that is being used. Examples of an

organic solvent include N,N-dimethylformamide and N,N-dimethylacetamide. Examples of an inorganic solvent include zinc chloride aqueous solution, rhodanide aqueous solution, nitric acid and sulfuric acid. The AN-based polymer is dissolved into one of these good solvents, and the uranium adsorbing material is then dispersed therein, with the ratio of AN-based polymer to good solvent being 1 to 20% by weight, and the ratio of adsorption material being 1 to 30% by weight.

The coagulation solution is a poor solvent that is able to cause coagulation and deposition of AN-based polymer from the slurry dope; any is acceptable as long as it is sufficiently miscible with the good solvent used in the slurry dope. Water is preferred, because the obtained adsorption material will then have affinity for water.

It is possible to use water alone as the coagulation solution, but the use of a mixture of a small amount of good solvent with the poor solvent is preferred in view of the strength and form of the thus-manufactured adsorption material. The composition of a coagulation solution preferably has a ratio of good solvent to poor solvent ranging from 1:0.5 through 1:7 by volume. The ratio of coagulation solution to slurry dope is preferably 5:1 or greater by volume, in view of the strength and form of the adsorption material, in the same fashion.

According to the present invention, the adsorption material is suitable for collecting uranium from a solution where a low

concentration of dissolved uranium is present, and it is particularly effective for collecting uranium from a solution where dissolved uranium is present in trace amounts when uranium is leached out of a low-grade uranium ore.

Working examples of the present invention are explained below. /3

Working Example 1

14 parts of metatitanic acid with grain diameter of 200 mesh were uniformly dispersed in 48 parts N,N-dimethylformamide (DMF). Separately, 4 parts of a copolymer of 97% by weight AN and 3% by weight vinyl acetate was dissolved in 34 parts of DMF. Both were mixed together to form a slurry dope having a uniform composition.

Separately, a mixed solution of 130 parts DMF and 350 parts water was prepared as a coagulation solution. This was mixed at 1000 rpm, and the slurry dope was added into this at a rate of 5 ml/min. The coagulated matter was water-washed in detergent liquid until cloudiness was no longer observed, giving an adsorption material. The metatitanic acid content of the adsorption material was 70% by weight. The adsorption material was packed into a column (2 cm internal diameter, 50 cm high), and a solution containing uranium (uranium concentration 4.0 mg/l, pH 8.2) as uranyl tricarbonate complex anions ($\text{UO}_2(\text{CO}_3)_3^{4-}$) was loaded into the column. As a result, 24 mg of uranium was adsorbed per 1 g of adsorption material. Then a 0.5 normal hydrochloric acid aqueous solution was allowed to flow, and 98% of the adsorbed uranium amount was eluted and recovered.

After elution, adsorption of the same uranium solution was again performed, resulting in adsorption of 23 mg uranium per 1 g adsorption material. The metatitanic acid content in the adsorption material did not change before and after these adsorption/elution operations.

Working Example 2

The adsorption material obtained in Working Example 1 was immersed in the same uranium solution as was used in Working Example 1, and this was stirred. After 12 hours, 25 mg of uranium was adsorbed per 1 g of adsorption material. The metatitanic acid content in the adsorption material did not change before and after this adsorption/elution operation.

Working Example 3

The adsorption material obtained in Working Example 1 was packed into a column as in Working Example 1, and a solution containing uranyl sulfate complex anions (uranium concentration: 5 mg/L, pH 3.0) was loaded into this column. As a result, uranium was adsorbed at a ratio of 23 mg uranium per 1 g adsorption material. Then elution was performed by causing an aqueous solution of 1 mole/liter sodium carbonate to flow into the adsorption material onto which uranium had been adsorbed, resulting in the recovery of 70% of the amount of adsorbed uranium. The lead sulfide [sic] content in the adsorption material did not change before and after these adsorption/elution operations.

Working Example 4

An adsorption material was obtained by an operation identical to that of Working Example 1, with the exception that lead sulfide was used instead of the metatitanic acid that had been used to manufacture the adsorption material in Working Example 1. The lead sulfide content of the adsorption material was 65% by weight. The adsorption material was packed into a column, and a uranium adsorption test, identical to that adsorption operation of Working Example 1, was performed. As a result, uranium was adsorbed at a ratio of 11 mg per 1 g of adsorption material.

The uranium was then eluted by pouring a sodium carbonate aqueous solution onto the adsorption material onto which uranium had been adsorbed at a rate of 1 mole/liter. As a result, 60% of the adsorbed uranium was collected. The lead sulfide content in the adsorption material did not change before and after these adsorption/elution operations.

Working Example 5

An adsorption operation identical to that of Working Example 2 was performed, with the exception that the adsorption material obtained in Working Example 4 was used instead of the adsorption material of Working Example 2. As a result, uranium was adsorbed at a rate of 12 mg uranium per 1 g adsorption material. The lead sulfide content in the adsorption material did not change before and after these adsorption/elution operations.

Working Example 6

An adsorption material was prepared identical to that of Working Example 1, with the exception that basic zinc carbonate was used to prepare the adsorption material instead of the metatitanic acid of Working Example 1. The basic zinc carbonate content of this adsorption material was 68% by weight. This adsorption material was mixed into a uranium solution using the uranium adsorption operation of Working Example 1. After 12 hours, uranium had been adsorbed at a ratio of 10 mg of uranium per 1 g of adsorption material. The basic zinc carbonate content in the adsorption material did not change before and after these adsorption/elution operations.

Working Example 7

A slurry dope and coagulation solution were prepared having compositions identical to those used in the preparation of the adsorption material of Working Example 1. These 2 fluids were guided to a two-fluid nozzle, and under shearing conditions, a metatitanic acid and a copolymer containing the slurry dope were coagulated into a fibrous form, so as to make an integrated material, thus manufacturing an adsorption material. The metatitanic acid content in this adsorption material was 71% by weight.

This fibrous adsorption material was immersed in a solution containing uranyl tricarbonate complex anions (uranium concentration: 2 mg/liter, pH 7.6) for 10 hours. This was then eluted with 1

moles/liter of sodium carbonate aqueous solution, with the recovery of 22 mg of uranium per 1 g of adsorption material.

Working Example 8

The adsorption material of Working Example 7 was immersed for 12 hours in a solution that contained uranyl sulfate complex anions (uranium concentration: 3 mg/liter, pH 2.7). This was then eluted with 1 mole/liter of sodium carbonate, and 22 mg/liter uranium was collected per 1 g of adsorption material.